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13. ABSTRACT (Maximum 200 words)

Widespread application of carbon-carbon composites has been restricted by their low oxidation resistance at elevated temperatures. A major barrier to the development of protective ceramic coatings for these materials is the lack of experimental methods for depositing adherent, crack-free, protective ceramic deposits with high deposition rates in a cost-effective manner. The objective of this project is to develop dense, adherent, electrophoretically deposited ceramic coatings on carbon-carbon composites, giving rise to enhanced oxidation and wear resistance. Ceramic materials, coating additives and methods for bonding and densifying the selected materials have been identified. A broad range of ceramic materials were successfully deposited on carbonaceous substrates from a non-aqueous deposition bath using the electrophoretic technique. Deposited ceramic layers were bonded using either an organometallic polymeric binder or an inorganic phosphate-based binder. Attempts to densify the ceramic coatings were unsuccessful.

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1. INTRODUCTION

Carbon-carbon composites, a relatively new class of materials, have been receiving increasing interest as structural components capable of withstanding very high temperatures in the aerospace industry (1). The composites consists of continuous, or discontinuous, graphite fibers [produced from one of three precursor materials: rayon, polyacrylonitrile (PAN) or petroleum pitch] in a carbonaceous matrix. The latter is formed either by the carbonization of an impregnated organic liquid (or solid) or by the deposition of pyrolytic carbon on infiltrating the graphite fibers with a hydrocarbon vapor at elevated temperatures. Because of the excellent control over the directionality of the graphite fibers, the mechanical properties of carbon-carbon composites can be readily tailored (2).

Carbon-carbon composites have significant strength at temperatures in excess of 5000°F (2760°C), well above the melting point of most other materials (1,2). Their coefficient of thermal expansion is low: $0.3\text{--}1.9 \times 10^{-6}$ in/in/°F ($0.54\text{--}3.5 \times 10^{-6}$ cm/cm/°C), so that they remain dimensionally stable over a wide temperature range. Advanced carbon-carbon (ACC) composites (made from continuous PAN-derived fibers, in conjunction with four resin-impregnation and pyrolyzation treatments) are stronger and stiffer than conventional carbon-carbon composites (made from rayon-derived fibers, in association with three resin-impregnation and pyrolyzation treatments) (1,2). ACC composites have tensile strengths of over 300,000 psi (2,100 MPa), five times that of steel, while they are stiffer than titanium, with moduli up to 50,000,000 psi (340,000 MPa) (1). They are being used in products such as the nozzle in the F-100 jet engine afterburner and rocket nozzle exit cones [where flame temperatures approach 6000°F (3315°C)], turbine wheels operating at greater than 40,000 RPM, non-wetting crucibles for molten metals, nosecones and leading edges for missiles and the space shuttle orbiter, wind tunnel models and disc brakes for racing cars and aircraft (1-3).

Although the high-temperature mechanical and physical properties of carbon-carbon composites have led to their increasing use as refractory materials in the aerospace industry, their widespread application has been restricted by the low oxidation resistance of carbonaceous materials at elevated temperatures. The oxidation threshold for carbon-carbon composites $\sim 700^\circ\text{F}$ ($\sim 370^\circ\text{C}$) can be raised to $\sim 1110^\circ\text{F}$ ($\sim 600^\circ\text{C}$) by the incorporation of refractory particulates (B, Si, Zr, Hf, etc.) within the bodies of the composites (4). A major hindrance in the development of protective ceramic coatings leading to the formation of oxidation-resistant composites is the lack of experimental methods and techniques for depositing adherent, crack-free, protective ceramic deposits with high deposition rates in a cost-effective manner. The two techniques widely used at present include the pack-cementation process (5,6) and chemical vapor deposition (CVD) (7). Carbon-carbon composites used in the nosecone and leading edges of the wings in the space shuttle orbiter are coated with a ceramic deposit by means of the former technique (5,6). Composite components are packed in a mixture of SiC, Al_2O_3 and Si and subjected to a thermal treatment at $\sim 3000^\circ\text{F}$ ($\sim 1650^\circ\text{C}$) in an Ar atmosphere. The outer layers of the composites are converted to SiC to a depth of 0.02–0.04 in (0.05–0.10 cm). However, on cooling, the SiC layer develops microcracks, so that additional oxidation protection is needed. Five pressure impregnation cycles, with tetraethylorthosilicate (TEOS), followed by heating at 600°F (315°C) deposits SiO_2 in the pores of the SiC-coated composites, greatly enhancing the oxidation protection of the substrates.

Chemical vapor deposition (CVD) processes have been developed to produce single- and multi-layered ceramic coatings on various substrates that approach theoretical densities (8,9). However, coatings derived from these processes, in many cases, suffer from poor adhesion, low deposition rates ($1 \mu\text{m hr}^{-1}$), the inability to grow thick deposit layers, the

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development of microcracks and unsatisfactory oxidation and wear protection, particularly at high temperatures (7-9).

Electrophoretic deposition has a number of unique features, in contrast to other coating deposition methods, e.g., plasma spraying or CVD (10). These include greater deposit uniformity, the ability to obtain reproducible thicknesses and extremely smooth deposits. The throwing power is excellent, because, as the coating deposits on projecting edges, the insulating effect of the coating causes the current to shift to remote areas and recesses. The method is rapid; for example, coatings of 2-4 mils in thickness can be applied in 20 seconds or less (10). Since particles are deposited, rather than individual ions, a large amount of material can be deposited for a small amount of electrical charge consumed. An appealing feature of the technique is that the wasting of expensive coating materials, as encountered, for instance, in plasma spraying operations, is eliminated. A particularly attractive aspect of the electrophoretic technique is that it facilitates the codeposition of ceramic fibers in an undamaged fashion, along with ceramic powder particles, leading to ceramic fiber-reinforced ceramic matrix coatings, which cannot be achieved with CVD or plasma spraying methods. Further, the codeposition of ceramic coating "dopants," e.g., sintering aids, can be readily accomplished.

Although electrophoretic deposition is an efficient, economical and simple method of depositing ceramic coatings from particulate suspensions on electrically conducting substrates, e.g., ACC composites, the as-deposited coating layers formed lack the necessary adhesive and cohesive characteristics required in practical applications. Various approaches for bonding ceramic particles together and to substrates have been developed. These include: (i) sintering at high temperatures, either in the presence, or absence, of small amounts of added sintering aids; (ii) reactive bonding with phosphate-derived materials (refractory cements), and (iii) the use of refractory glasses, e.g., borosilicate- and phosphate-based glasses as binding matrices. Most of these methods for "densifying" ceramic particulate coatings, although requiring elevated or high-temperature treatments, are rather well understood.

Commercial applications of the electrophoretic deposition process, at present, include the deposition of the primer paint layer onto treated automobile bodies (11), formation of rubber gloves by electrophoretic deposition of latex onto a mandrel (12), the deposition of enamel coatings onto metal substrates (13) and the electrophoretic forming of β -alumina ceramic parts (14).

Under contract DAAL03-90-C-0016 with the United States Department of Defense, Lynntech, Inc., had as a goal the development of an electrophoretic ceramic coating process, in conjunction with post-deposition thermal treatments, to deposit dense, adherent, crack-free, erosion-resistant, protective ceramic coatings on carbon-carbon composites. The aim of the project was to overcome the inherent reactivity of carbon-carbon composites toward oxygen, particularly at temperatures greater than 1830°F (1000°C). The realization of a cost-effective, high deposition rate process, rendering carbon-carbon composites oxidation- and erosion-resistant at temperatures up to 4000°F (2200°C) would have great significance in aerospace technologies, as well as in other industrial applications.

This report outlines research work carried out to establish concept feasibility. Laboratory-scale ceramic coating experiments were performed using graphite substrates and a methanol-based, silicon carbide-containing, electrophoretic deposition bath. Hexane solutions of polycarbosilane and aqueous phosphoric acid solutions of aluminum phosphate were used for binding electrophoretically deposited ceramic coatings. Hard,

adherent coatings were obtained after contacting the ceramic coatings with either of these solutions and subsequently thermally treating them in an inert atmosphere at 500°C. Attempts at further densification of ceramic deposits on heating in an argon atmosphere at temperatures up to 2150°C were unsuccessful.

2. BACKGROUND

Matrix-inhibited, high-performance ACC composites have an oxidation threshold temperature of the order of 1110°F (600°C) (4,15). A number of factors have to be considered in identifying likely ceramic coating materials that have the potential to be successful in protecting ACC composites in oxidizing erosive environments.

1. **Mechanical Compatibility:** Good mechanical compatibility between the ceramic coating and the carbon-carbon substrate is the key factor in determining the coating/substrate system performance. Mechanical compatibility is determined by the closeness of the match between the thermal expansion coefficients (TEC) of the refractory ceramics and the carbon-carbon materials. From the data presented in Figure 1, silicon-based ceramics display the best thermal expansion compatibility with carbon-carbon materials and exhibit the lowest oxidation rates of the high-temperature ceramics.

2. **Useful Protective Temperature Range of Ceramic Coatings on Carbon:** This can be defined by the limiting-use temperature at the upper end of the temperature range and by the micro-cracking temperature observed on cooling at the lower end of the temperature range (4). Recent experimental work (16,17) has shown that for coatings of SiC and Si₃N₄, the upper-use temperature occurs at 3180–3270°F (1750–1800°C), as a result of detrimental interfacial reactions between the formed SiO₂ scale and the underlying ceramic. A similar upper use-limiting temperature has also been observed for MoSi₂ (4). The lower end-use temperature for silicon-containing ceramics, e.g., Si₃N₄ and SiC [~ 2280°F (~ 1250°C)] (4), is determined by the temperature at which coating "self-healing effects" associated with the formation of coating oxidation products are no longer able to repair coating micro-cracks developing at or below this temperature on cooling. In the intrinsic protective temperature range of silicon-based ceramic coatings (2010–2280°F to 3180–3270°F), microcracks developed at lower temperatures can be sealed (at least, partially) by oxidation products derived from the coatings.

Candidate protective ceramic coatings for advanced carbon-carbon composites can be divided into those coating systems utilizing silicon-based ceramics (e.g., SiC and Si₃N₄) which are very compatible mechanically but are temperature-limited to values lower than 3180°F (1750°C) and those less well-defined systems based on other ceramic materials for higher-temperature applications.

Reaction-sintered ZrC and ZrB₂ coatings on carbon have been observed to be protective against oxidation for short times at temperatures up to 4000°F (2200°C) (18). The most oxidation-resistant ceramic materials at temperatures higher than 3180°F (1750°C) that have been identified are HfB₂ and mixtures of HfB₂ and SiC (19,20). However, the high oxidation rates of these refractory carbides and borides preclude their use for long-term oxidation protection of carbon-carbon composites above 3180°F (1750°C) [100 hours at 3500°F (1930°C) would produce almost 0.08 in (0.2 cm) of oxide on the best HfB₂-SiC material (19,20)]. Oxide materials offer the best promise, where the criteria for selection would include melting points, vapor pressures and thermal expansion coefficients (4). From the vapor pressure data, presented in Figure 2, ZrO₂, HfO₂, Y₂O₃ and ThO₂ have the required thermal stability for long-term use at temperatures up to 4000°F (2200°C). Also, Al₂O₃ may be useful for shorter exposure times at these high temperatures. A key

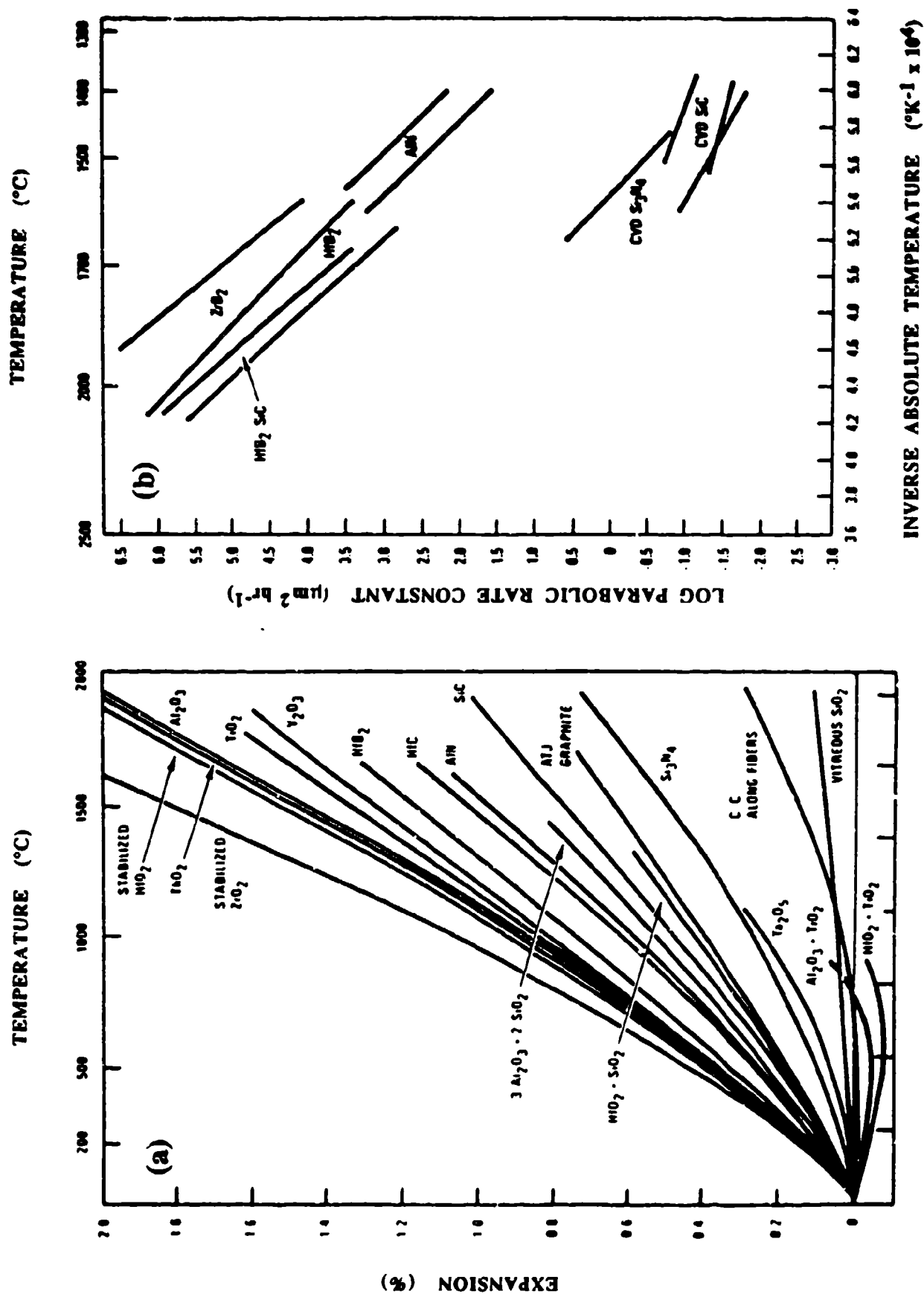


FIGURE 1 (a). Thermal expansion characteristics of selected refractory materials.

(b). Oxidation rates of selected high temperature ceramic materials.

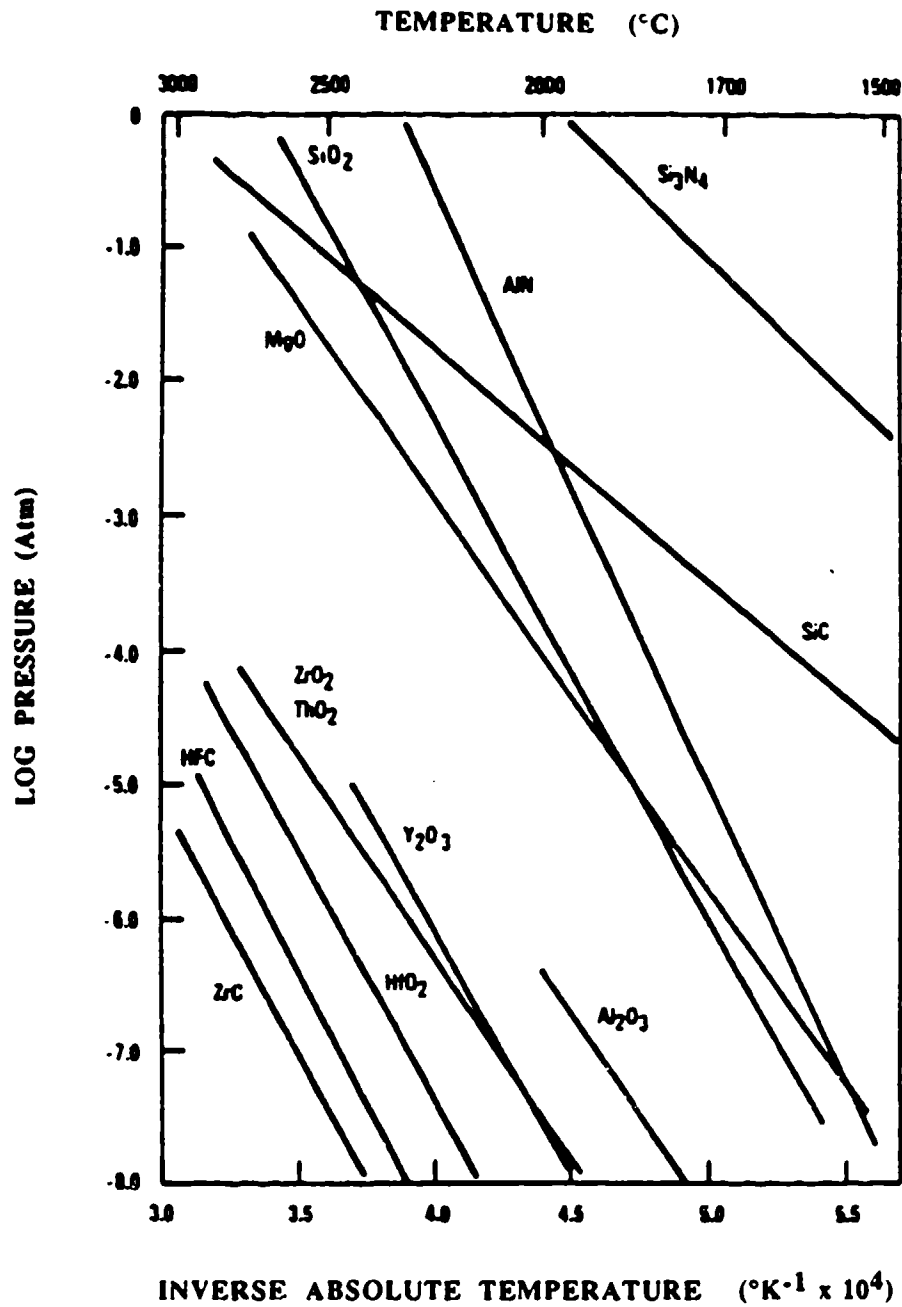


FIGURE 2. Vapor pressures of various high temperature ceramics.

factor concerning the former list of oxide materials, in addition to their mechanical incompatibility (cf., Fig. 1), is that they have very high oxygen permeabilities (21); hence, they are not likely to form effective oxygen barriers at the high temperatures encountered. Functional protective ceramic coating systems for these high-temperature applications will have to be multi-layered coatings, consisting of inner carbide and boride layers and outer oxide layers, taking into account the need for carbon (and carbide), as well as oxygen (and oxide) diffusion and permeation barriers.

3. Technology to Seal Developed Micro-Cracks in Ceramic Coatings in the Temperature Range 1100°F (600°C) to the Micro-Cracking Temperatures: In order to develop ceramic coatings which protect carbon-carbon composites over the whole accessible temperature range, micro-cracks formed by thermal stresses require the incorporation of sealants to provide protection below the micro-cracking temperature values. Surface-applied sealants, based on B_2O_3 , are generally useful for only limited time periods at high temperatures, due to their volatilization [less than 10 hours at 2370°F (1300°C)] (4). All ceramic coating systems which have rendered a degree of oxidation protection to carbon-carbon composites for certain periods of time at temperatures up to 2730°F (1500°C) incorporate boron, or boron compounds, in some fashion (either within the carbon-carbon materials, as a modifier on the carbon fibers, or as a component in the coating systems (4). To provide full range protection for temperatures up to 3180°F (1750°C), where silicon-based ceramic coatings can still be used, SiO_2 glasses may provide an alternative to borate glasses, provided precautions are taken to prevent SiO_2 from reacting with carbon. It is known that the stability limit of SiO_2 on SiC is ~ 3180°F (~ 1750°C) and that carbide layers provide enhanced wetting of SiO_2 glasses, compared to the glasses on carbon (4,16).

4. Characteristics of the External Layers of Protective Ceramic Coatings: The outer regions of protective ceramic coatings must: (i) provide an effective barrier to the inward diffusion of oxygen, and (ii) possess low volatility, to prevent excessive erosion in high-velocity gas streams.

5. Characteristics of the Internal Layers of Protective Ceramic Coatings: The internal layers of the coating must: (i) provide good adherence to the carbon-carbon substrate without excessive substrate penetration, and (ii) prevent outward carbon diffusion, at least to the extent of preventing carbothermic reduction reactions in the external layers.

3. PHASE I TECHNICAL OBJECTIVES

The overall objective of the project was to develop dense, adherent, electrophoretically deposited ceramic coatings on ACC composites, giving rise to enhanced oxidation and wear resistance.

The specific objectives of the Phase I research were:

1. Electrophoretically deposit particulate and fibrous SiC on ACC composites from methanol-based suspension baths, both in the presence, and absence, of inorganic and organic additives.
2. By means of low-temperature reactive phosphate bonding and high-temperature sintering, bond and densify electrophoretically deposited SiC ceramic coatings on ACC composites.

3. Determine in a preliminary manner the degree of oxidation and wear protection provided to ACC composites by bonded and densified electrophoretically deposited SiC coatings.
4. Using scanning electron microscopy, investigate the degree of surface smoothness, the appearance of thermally induced micro-cracks on thermal cycling and the nature of the composite/coating interface for bonded and densified electrophoretically deposited SiC coatings on ACC composites.

4. ORGANIZATION OF REPORT

In this Phase I report, the work performed, the results obtained and a discussion of their significance for the intended application are outlined in the following three sections. A description of the materials and procedures used for the deposition of ceramic coatings is given in the next section. Electrophoretic deposition characteristics of ceramic coatings using various ceramic materials are described in Task 1. Under Task 2, approaches undertaken for bonding and densifying electrophoretically deposited coatings are presented.

5. MATERIALS AND PROCEDURES USED FOR THE ELECTROPHORETIC DEPOSITION OF CERAMIC COATINGS

The various ceramic materials, chemicals and solvents, and their suppliers, used for the electrophoretic deposition of ceramic coatings are outlined in Table 1. Since silicon carbide was selected as the ceramic coating material to be used, a number of different forms of the material were obtained and characterized prior to electrophoretic deposition studies. Scanning electron micrographs of powdered silicon carbide, supplied by Cerac, Inc., and by Third Millenium Technologies, Inc., are given in Figures 3 and 4, respectively. The former material exhibits a platelet-like configuration, having an average particle size of approximately 8 μm , while the latter is spherical-like in shape with submicron dimensions (average particle size of the order of 0.4 μm). Characteristics of the silicon carbide powder, supplied by Cerac, Inc., include: (i) a carbon content (found) of 29.48%, as compared to a carbon content (theoretical) of 29.95%, and (ii) a crystal structure consisting of a mixture of predominantly (approximately 70%) hexagonal β -SiC and several hexagonal/rhombohedral forms of α -SiC. An X-ray diffractogram, derived from this silicon carbide powder is presented in Figure 5. Peaks in the XRD pattern obtained have been assigned to the α -SiC and β -SiC polymorphs.

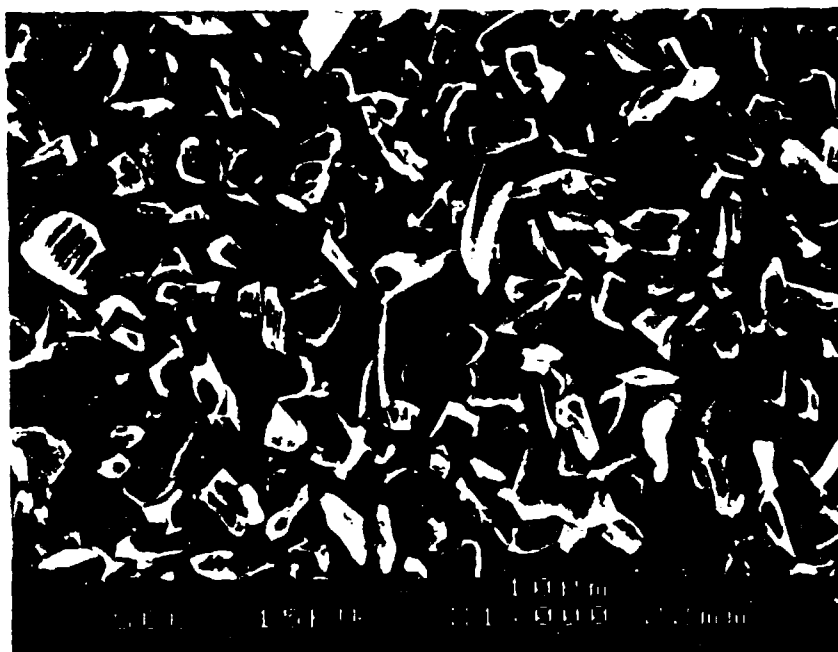
Scanning electron micrographs of silicon carbide whiskers, supplied by Third Millenium Technologies, Inc., are presented in Figure 6. From the micrographs, it can be seen that the whiskers possess an average diameter of about 1.5 μm and an average length of the order of 20 μm . Scanning electron micrographs of powdered boron carbide, also supplied by Third Millenium Technologies, Inc., are given in Figure 7. Examination of this figure reveals an average particle size of the order of 5 μm . Aluminum metal powder (average particle size, 6 μm) and submicron boron metal powder (average particle size, 0.1 μm) were also obtained from Alcoa and Noah Technologies, respectively.

Two ceramic coating binder materials were investigated in this project. The first, an inorganic-based material, consisted of a concentrated aluminum phosphate solution in aqueous phosphoric acid. This binder material was supplied by RMCI Southeastern, Pennsylvania. The second material, polycarbosilane, an organometallic polymeric compound, was obtained from Dow Corning, Midland, Michigan. The polycarbosilane supplied in the form of pale yellow lumps is highly soluble in hexane and has a melting

TABLE 1. MATERIALS AND SUPPLIERS USED FOR THE ELECTROPHORETIC DEPOSITION OF CERAMIC COATINGS

MATERIAL	CHEMICAL	FORM	SUPPLIER
Silicon Carbide	SiC	Powder; 8 μm average particle size	Cerac, Inc. Milwaukee, WI
Silicon Carbide	SiC	Submicron powder; average particle size 0.4 μm .	Third Millenium Tech. Knoxville, TN
Silicon Carbide	SiC	Whiskers; 1.5 μm in diameter and 20 μm in length	Third Millenium Tech. Knoxville, TN
Boron Carbide	B ₄ C	Powder; 5 μm average particle size	Third Millenium Tech. Knoxville, TN
Aluminum Metal	Al	Powder; 6 μm average particle size	Alcoa Pittsburgh, PA
Boron Metal	B	Submicron powder; average particle size 0.1 μm	Noah Technologies San Antonio, TX
Aluminum Phosphate	Al(H ₂ PO ₄) ₃	Aqueous phosphoric acid solution	RMCI Southeastern, PA
Polycarbosilane	(R ₁ R ₂ Si-CH ₂ -SiHR ₃) _n	Solid lumps	Dow Corning Midland, MI
Aluminum Chloride	AlCl ₃ • 6H ₂ O	Solid crystals	Fisher Scientific Pittsburgh, PA
Methanol	CH ₃ OH	Liquid	Fisher Scientific Pittsburgh, PA
Graphite	C	Solid, ATJ grade	Union Carbide Cleveland, OH
Graphite	C	Solid	Poco Graphite Decatur, TX

(a)

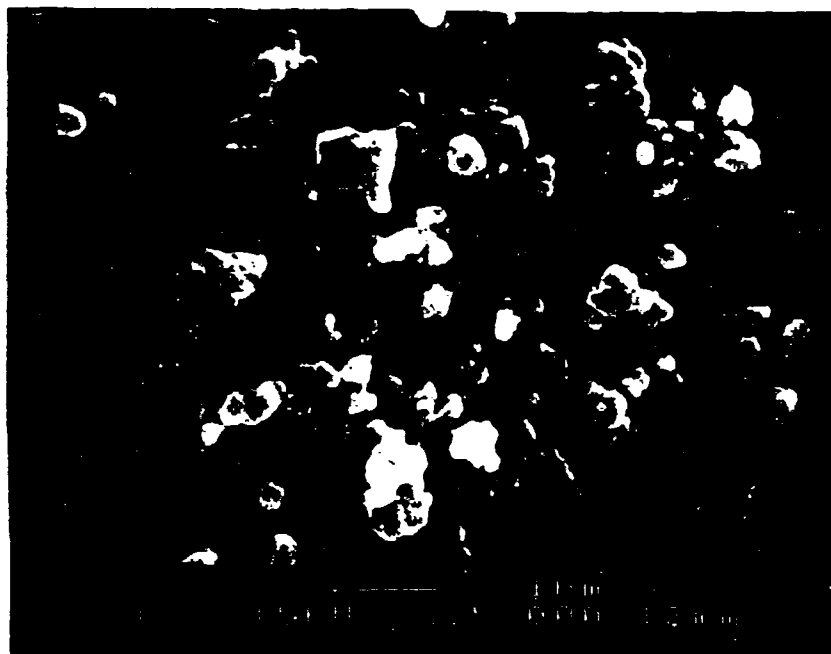


(b)



FIGURE 3. Scanning electron micrographs of powdered SiC supplied by CERAC, Inc. (Stock No.: S-1058).

(a)



(b)

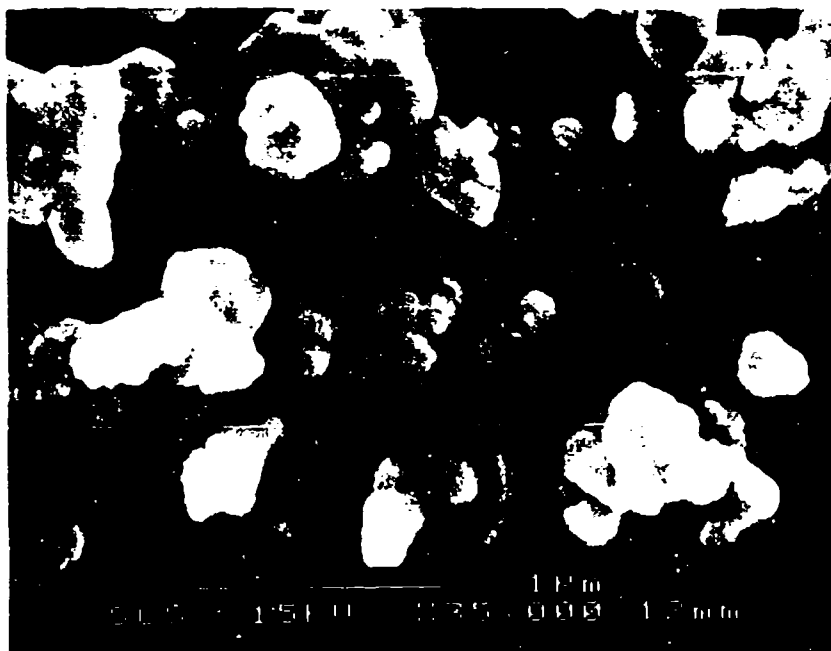


FIGURE 4. Scanning electron micrographs of powdered SiC supplied by Third Millenium Technologies, Inc.

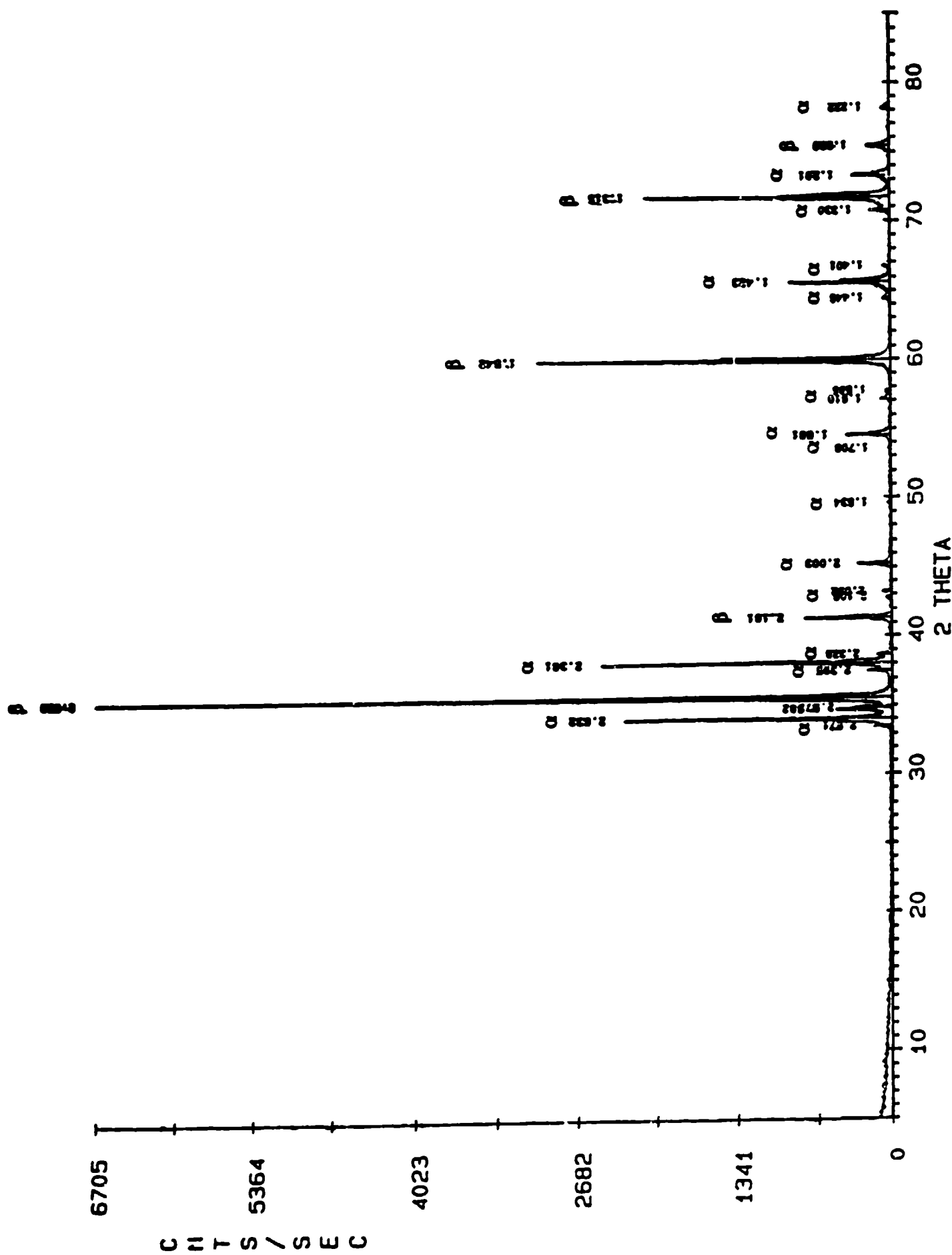
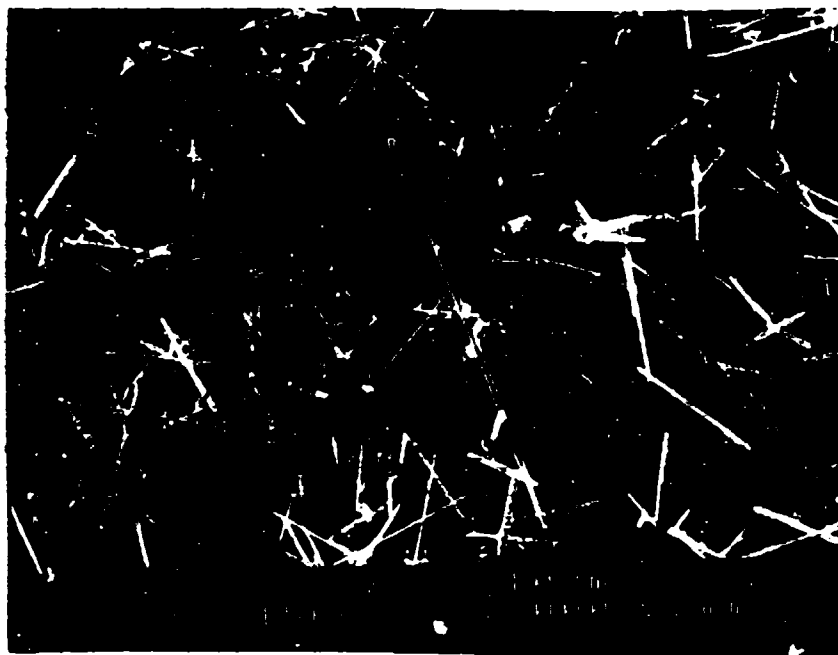


FIGURE 5. X-ray diffractogram of powdered SiC supplied by CERAC, Inc. (Stock No.: S-1058).

(a)



(b)

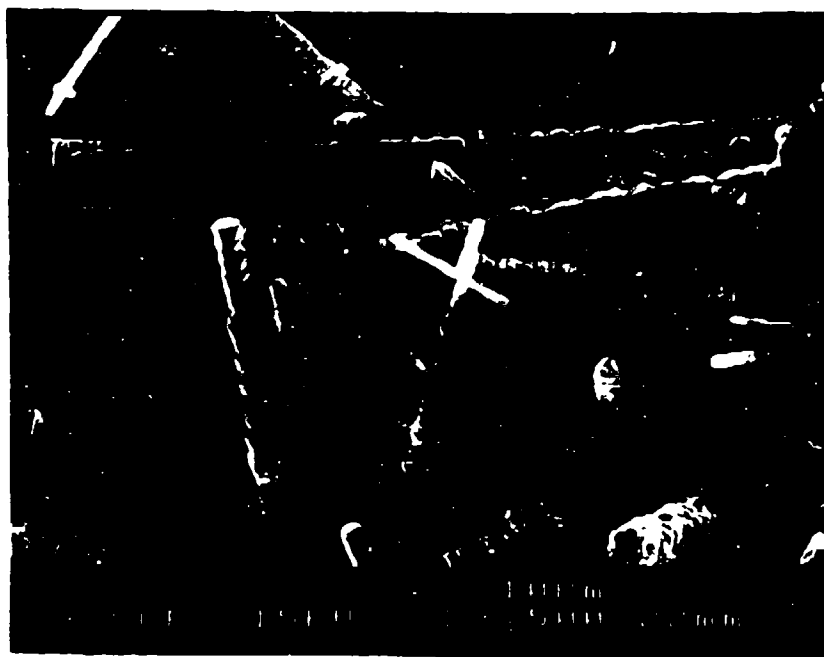


FIGURE 6. Scanning electron micrographs of SiC whiskers supplied by Third Millenium Technologies, Inc.

(a)



(b)



FIGURE 7. Scanning electron micrograph of powdered B_4C supplied by Third Millenium Technologies, Inc.

point in the temperature range 195°C–220°C. The polymeric compound has applications as a precursor ceramic material. On pyrolyzing in excess of 1000°C in an inert atmosphere, the material gives a significant yield (58%–63%) of silicon carbide, indicative of its role as a binder for electrophoretically deposited SiC-based ceramic coatings.

In the proof-of-concept experiments carried out in this Phase I project, graphite substrates were used instead of carbon-carbon composites, because of their ready availability. Two grades of graphite were used, ATJ grade from Union Carbide Corporation and an unspecified grade from Poco Graphite. Graphite substrate dimensions were 2" x 1" x 0.125" in the case of Poco Graphite and 2" x 1" x 0.25" for ATJ-grade graphite. Prior to being used for electrophoretic deposition studies, graphite substrates were cleaned, washed in isopropanol and air-dried at approximately 110°C.

Common chemicals and solvents required for carrying out the electrophoretic deposition experiments were purchased from suppliers of research chemicals, e.g., Fisher Scientific and Aldrich Chemical Company.

The electrophoretic deposition bath used consisted of 500 ml of methanol to which was added 5 ml of ultrapure water, 0.1 g of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and 12 g of particulate and/or fibrous ceramic materials, e.g., silicon carbide, boron carbide, boron, carbon or aluminum. The addition of dissolved polycarbosilane in hexane to methanol-based silicon carbide-containing electrophoretic deposition baths proved to be unsatisfactory for the subsequent deposition of silicon carbide on graphite substrates. After performing initial experiments, this addition was not carried out in later electrophoretic depositions.

The experimental set-up and procedure used was as follows. A previously cleaned and weighed rectangular working graphite coupon was inserted between two externally connected graphite plate counter electrodes in a parallel arrangement. With the negative terminal of the DC power supply connected to the working graphite electrode and the positive terminal attached to the shorted counter electrodes, the power supply was switched on and the supported electrodes were immersed in the stirred silicon carbide-based suspension. All depositions were carried out at room temperature in air atmosphere. On completion of an electrophoretic deposition run, a coated graphite coupon was removed slowly from the deposition bath with the power supply on. After turning off the power supply, coated samples were removed from the electrode holder and allowed to dry in air overnight. Weights of deposited silicon carbide were obtained and deposit weights per unit area (mg cm^{-2}) were calculated.

6. TASK 1: ELECTROPHORETIC DEPOSITION OF SiC-BASED CERAMIC COATINGS ON GRAPHITE SUBSTRATES

Coating the external surfaces of graphite coupons from methanol-based plating baths containing refractory ceramic materials was carried out using the electrophoretic deposition technique. Examples of silicon carbide-coated graphite coupons, together with uncoated coupons, are shown in Figure 8. Excellent coating uniformity with good throwing power, characteristic of electrophoretic deposits in general, is evident from the figure. An attractive feature is the high quality coating laid down on the sharp, non-rounded edges of the graphite coupons. However, in practical applications, these sharp edges would be rounded to prevent the build-up of localized stresses in ceramic coatings.

Using Cerac-supplied powdered silicon carbide, variations of SiC deposit weights per unit area with the current density used in the deposition process for a number of deposition times are presented in Figure 9. For all deposition times, silicon carbide

(a)

(b)

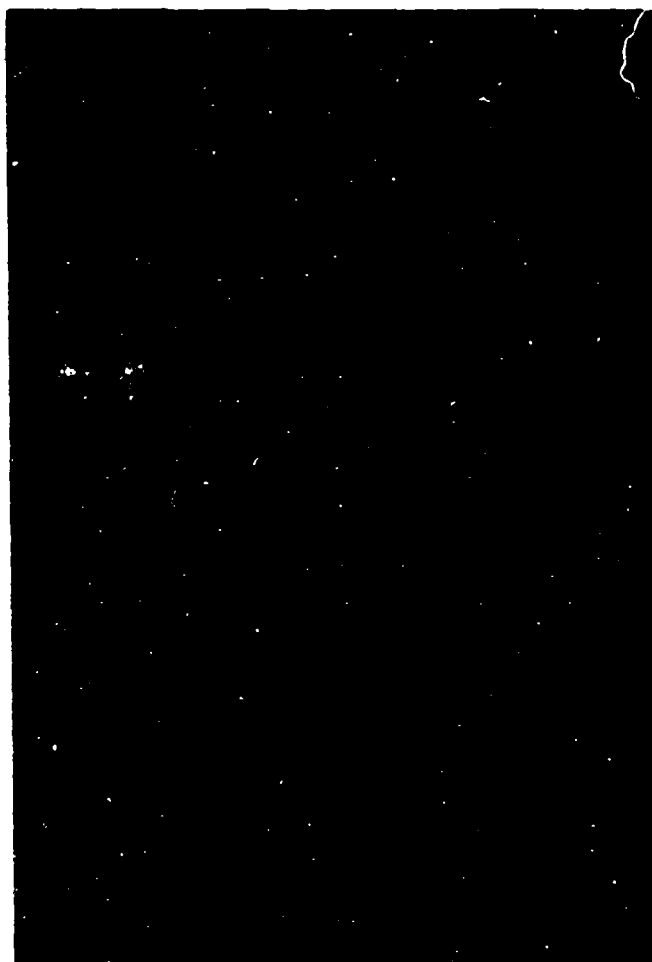


FIGURE 8 Electrophoretic deposits of silicon carbide on graphite substrates and similar uncoated substrates: (a) 4.0 mA cm^{-2} for 30 seconds, and (b) 6.0 mA cm^{-2} for 15 seconds

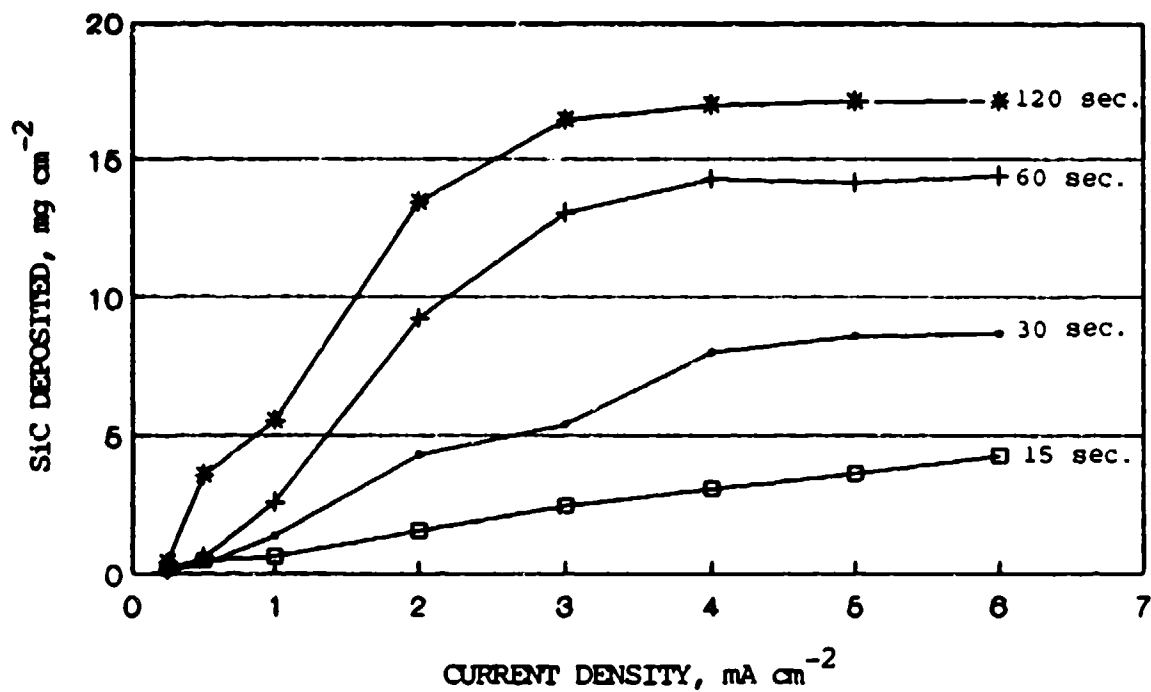


FIGURE 9. Variation of silicon carbide deposit weights per unit area of graphite substrates with current density for electrophoretically deposited coatings. Electrophoretic deposition bath contained 12 g of powdered SiC supplied by CERAC, Inc.

deposited per unit area increase in an almost linear manner with current density up to a value of 3 mA cm^{-2} . At higher current densities, a more gradual increase can be seen from the figure, finally levelling off at about 5 mA cm^{-2} . The best quality coatings were obtained at deposition times of 15–60 seconds with current densities of 4–6 mA cm^{-2} . For the longest deposition time (120 seconds) at these current densities, non-uniform streaky deposits were obtained.

Taking the theoretical density of silicon carbide (3.217 g cm^{-3}) and assuming the electrophoretically deposited coatings were 100% dense, deposit thicknesses of $30 \text{ }\mu\text{m}$ and $50 \text{ }\mu\text{m}$ can be obtained at a current density of 5 mA cm^{-2} , using deposition times of 30 and 60 seconds, respectively. Due to the high porosity of the as-deposited electrophoretic coatings, the actual thicknesses may be a factor of 1.5 higher.

Since it has been shown by other investigators that small additions (of the order of 1–2 wt %) of boron and carbon species to silicon carbide green bodies can significantly enhance densification processes, experiments were performed to determine the feasibility of obtaining satisfactory electrophoretic deposits on graphite substrates using deposition baths containing pure boron, pure carbon and a mixed particulate bath containing 96 wt % silicon carbide, 2 wt % boron and 2 wt % carbon. Two different carbonaceous powdered materials were investigated. A high surface area carbon, Vulcan XC-72R, from Cabot Corporation could not be deposited using the standard plating bath and experimental conditions. A battery-grade powdered graphite material from Lonza Graphite, however, was successfully deposited on graphite coupons.

Variations of deposit weights per unit area with current density for a number of deposition times on using pure boron, pure carbon and the mixed particulate-based electrophoretic deposition baths are presented in Figures 10–12, respectively. As observed for the Cerac-supplied powdered silicon carbide material (cf., Fig. 1), the amounts deposited per unit area increase almost linearly with current density, up to a value of 3 mA cm^{-2} . At current densities greater than this value, the increase in deposit weights is more gradual, finally reaching a plateau of about 5 mA cm^{-2} . For each deposition bath, excellent coating uniformity was observed. At the lower current densities, less than 1 mA cm^{-2} non-uniform coatings were obtained, while at the highest current densities used, e.g., 6 mA cm^{-2} , particularly at the longer deposition times (120 seconds), pits or small craters were observed on the surfaces of coatings. This latter phenomena is most likely due to the evolution of significant quantities of gas associated with electrochemical Faradaic reactions taking place at the surfaces of the graphite substrates. From these series of electrophoretic deposition experiments, it is clear that "doped" silicon carbide coatings (at least with boron and carbon) of high quality can be obtained using the electrophoretic approach.

Further studies on the range of ceramic materials that can be deposited from the methanol-based electrophoretic deposition bath were carried out. Two types of ceramic materials were investigated—silicon carbide whiskers having a whisker diameter of $1.5 \text{ }\mu\text{m}$ and a whisker length of $20 \text{ }\mu\text{m}$ and powdered boron carbide with an average particle size of $5 \text{ }\mu\text{m}$. Variations of deposit weights per unit area of graphite substrates with current density for a number of deposition times on using separately silicon carbide whiskers and powdered boron carbide in methanol-based electrophoretic deposition baths are presented in Figures 13 and 14, respectively. The results obtained are similar to those derived with previously described ceramic materials (cf., Figs. 9–12). At intermediate current densities and deposition times, excellent coating uniformity was observed, indicating good throwing power characteristics. It is clear from the deposition experiments carried out that a variety of individual and mixed ceramic materials, both powdered and in whisker form, can be

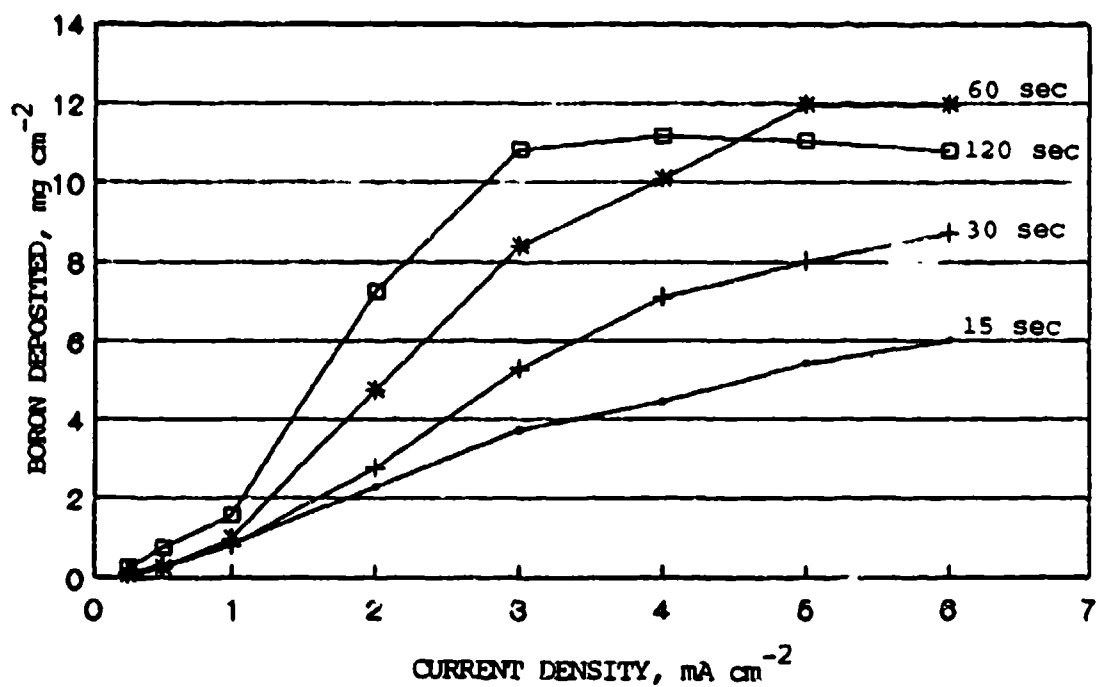


FIGURE 10. Variation of the weight of boron deposited per unit area of graphite substrates with current density for electrophoretically deposited coatings at four different deposition times. Electrophoretic deposition bath contained 12 g of powdered boron supplied by Noah Technologies.

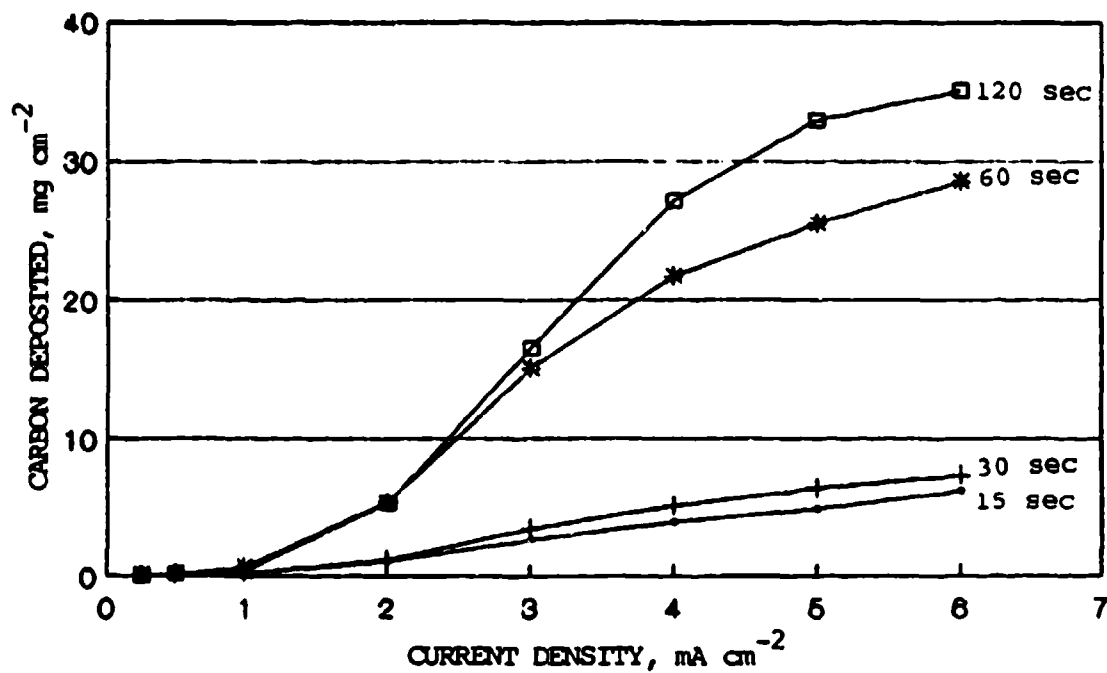


FIGURE 11. Variation of the weight of carbon deposited per unit area of graphite substrates with current density for electrophoretically deposited coatings at four different deposition times. Electrophoretic deposition bath contained 12 g of powdered carbon supplied by Lonza Graphite.

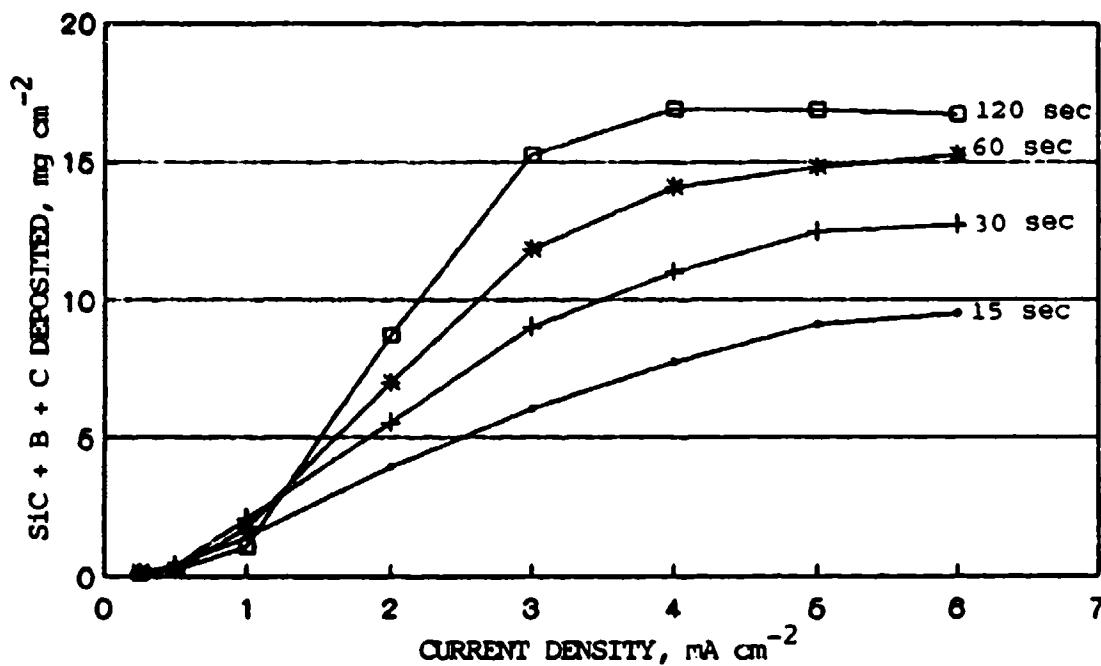


FIGURE 12. Variation of the weight of SiC + B + C deposited per unit area of graphite substrates with current density for electrophoretically deposited mixed coatings at four different deposition times. The composition of the bath in percent by weight of particulates was: SiC--96 wt %; B--2 wt %, and C--2 wt %. The total weight of particulates in the deposition bath was 12 g.

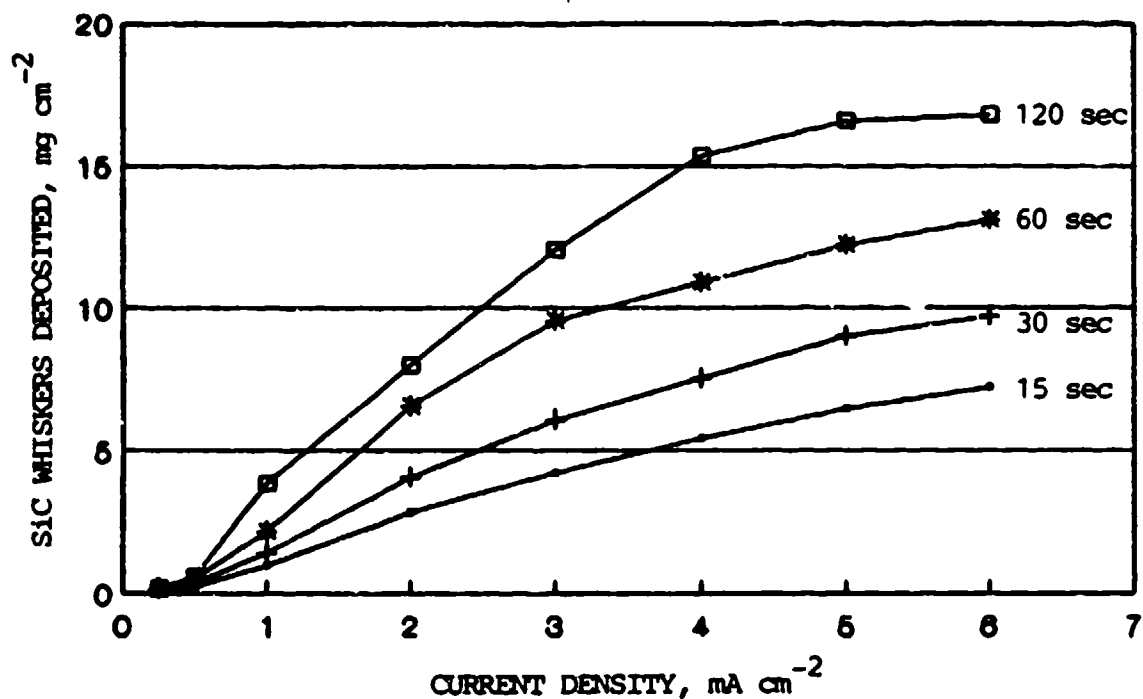


FIGURE 13. Variation of the weight of silicon carbide whiskers deposited per unit area of graphite substrates with current density for electrophoretically deposited coatings at four deposition times. Electrophoretic deposition bath contained 12 g of silicon carbide whiskers supplied by Third Millenium Technologies, Inc.

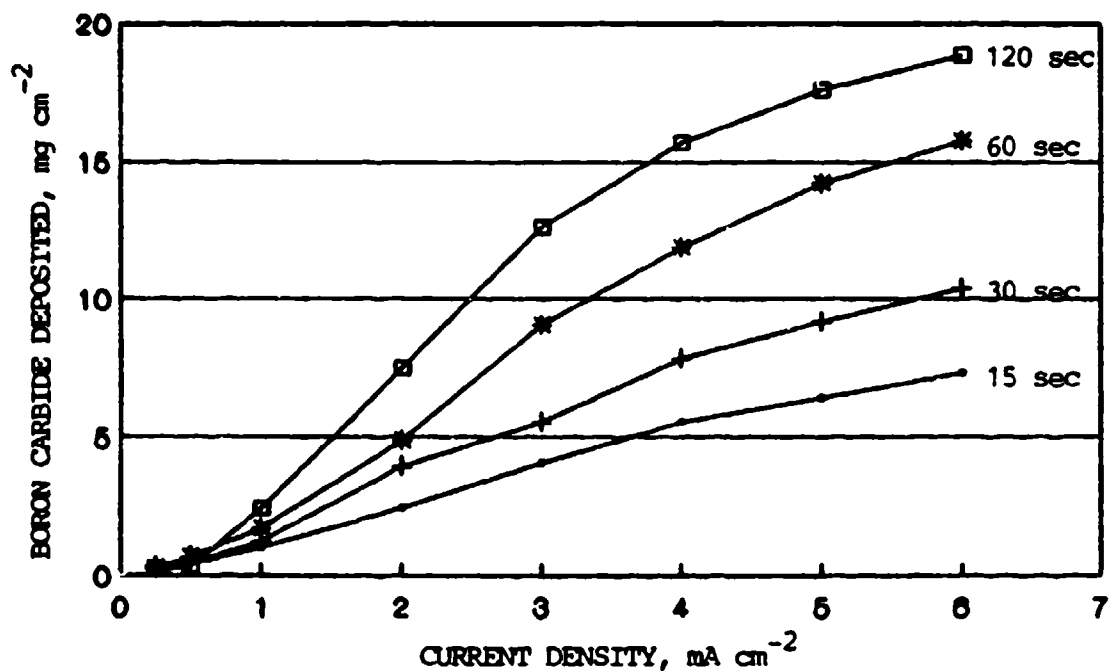


FIGURE 14. Variation of the weight of boron carbide deposited per unit area of graphite substrates with current density for electrophoretically deposited coatings at four deposition times. Electrophoretic deposition bath contained 12 g of boron carbide supplied by Third Millenium Technologies, Inc.

electrophoretically deposited on carbonaceous substrates using the electrophoretic deposition bath and experimental conditions developed in this project. On taking into account the complete range of ceramic materials deposited, optimum electrophoretic deposition conditions correspond to a current density of 3 mA cm^{-2} and a deposition time of 30 seconds. All subsequent depositions were carried out using these experimental parameters.

7. TASK 2: BONDING AND DENSIFYING ELECTROPHORETICALLY DEPOSITED CERAMIC COATINGS ON GRAPHITE SUBSTRATES

To obtain bonded and dense electrophoretically deposited SiC-based ceramic coatings on graphite substrates, three approaches were investigated in this project: (i) sintering at high temperatures in the presence of added sintering aids; (ii) reactive bonding with phosphate-derived materials, such as aluminum phosphate $[\text{Al}(\text{H}_2\text{PO}_4)_3]$, and (iii) formation of glassy matrices on heating codeposited glass precursors at elevated temperatures.

The incorporation of boron and carbon species into metal boride and metal carbide green bodies has a dramatic influence on both densification and grain growth during sintering (22). The carbon particles react with the oxygen-containing species on the surfaces of the ceramic particles to sufficiently reduce the oxygen levels in the very early stages of sintering (e.g., by CO evolution) to allow densification to proceed to completion. Also, both normal and exaggerated grain growth are inhibited by carbon addition, hence, promoting densification, since pore entrapment by grain boundary migration is minimized. Codeposition of submicron B_4C , along with SiC, was carried out to introduce a homogeneous distribution of boron species throughout the deposited ceramic coating. Subsequent immersion of electrophoretically deposited ceramic coatings in hexane solutions of polycarbosilane facilitated the binding (for ease of handling) of the particulate ceramic deposits and the introduction of a carbon species throughout the deposited coating on pyrolyzing at elevated temperatures in an inert atmosphere.

The starting material for the preparation of inorganic phosphate-based binding agents is often aluminum dihydrogen phosphate, $\text{Al}(\text{H}_2\text{PO}_4)_3$, which undergoes a setting reaction on coming in contact with the surface of basic oxides or condenses by thermal dehydration to $\text{Al}(\text{PO}_3)_3$ (23). At about 2370°F (1300°C), the crystalline $\text{Al}(\text{PO}_3)_3$ is converted into a molten glass, hence, its usefulness both as a binding and microcrack sealing agent. At still higher temperatures, the melt decomposes, releasing P_2O_5 and deposits AlPO_4 , which, at temperatures up to 3270°F (1800°C), is further converted into $\alpha\text{-Al}_2\text{O}_3$, again with release of P_2O_5 . These decomposition reactions are of considerable importance in the production of highly refractory materials (24). Phosphate-bonded ceramic materials do not show weak regions on heating, are highly refractory, have good abrasion resistance at high temperature and exhibit good slag resistance (25). In the present investigation, electrophoretically deposited SiC-based ceramic coatings on graphite substrates were reactively bonded as a result of being sprayed with and immersed in aluminum phosphate-based solutions, followed by thermal treatments in argon at temperatures in the range 400°C – 450°C .

Incorporation of various additives, e.g., B and Al, into SiC-based deposits can give rise to heterogeneous coatings in which a glassy matrix is formed upon heating the mixed powdered coating arising from the products of physical, chemical and physico-chemical interactions of the components with one another and atmospheric oxygen (26). Oxidation-reduction processes play an important role in the formation of such coatings. Ceramic coatings with a glassy matrix are characterized by a high degree of cohesiveness, heat

resistance, and strong adhesion to the substrate. Suitable glassy materials for such coatings are borosilicate glasses, containing more than 75 wt % of SiO_2 (26). They are very tough, have a relatively flat temperature dependence of viscosity, high resistance to crystallization and wet various materials. Further, they react weakly with a number of materials and can, therefore, exist in contact with them for a long time at high temperatures. In an attempt to obtain glassy matrix-based ceramic coatings, powdered boron and aluminum were separately codeposited with silicon carbide-based ceramic materials.

Electrophoretic bath compositions, deposition conditions and post-deposition treatments used to investigate the three approaches described above for bonding and densifying electrophoretically deposited SiC-based ceramic coatings on graphite substrates are presented in Table 2. The post-deposition treatments and high temperature sintering conditions utilized are outlined in more detail in Table 3. Preliminary experiments on the bonding of electrophoretically deposited powdered silicon carbide coatings using hexane solutions of polycarbosilane revealed that subsequent microcracking and delamination of the coatings on being cured at 400°C – 500°C in argon can be prevented on using a deposition bath containing SiC whiskers, as well as SiC powder. From Table 2, it can be seen that the same basic electrophoretic deposition bath was used in all experiments, but, in some instances, it also contained additives, such as B_4C powder, B powder and Al powder. Electrophoretically deposited ceramic coatings on graphite substrates were bonded using three procedures: (i) polycarbosilane solutions; (ii) aluminum phosphate solution, and (iii) aluminum paint. The experimental conditions used for each of these procedures is given in Table 3.

In the case of polycarbosilane solutions, the bonding of the electrophoretically deposited coatings involved immersion in three solutions of increasing polycarbosilane concentration, with intermediate air-drying and curing at 450°C in argon. With the aluminum phosphate solution, it was observed that initial immersion in this solution, led to a washing-off of the deposited ceramic coating. To overcome this problem, the phosphate solution was applied by means of placing the coated substrates in a mist of the solution derived from an atomizer, followed by drying and curing at 450°C in argon. After two such mist applications, coated substrates were then immersed into the aluminum phosphate solution itself, allowed to soak/dry in air and finally cured at 450°C in argon. Ceramic coatings, bonded by either of these procedures, were observed to be quite hard with good interparticle bonding and good adhesion between the graphite substrates and the ceramic deposits. Bonded coatings were found to be difficult to remove from the substrates and did not crack or delaminate on cutting cross-sections with a diamond saw. Aluminum spray-painted ceramic-coated graphite substrates could be easily handled but were found, as expected, not to have the same degree of bonding as derived from the other two procedures described above. Photographic views of ceramic-coated graphite substrates, bonded with polycarbosilane and aluminum phosphate are presented in Figures 15 and 16.

Scanning electron micrographs at various magnifications of the cross-section of a ceramic coating/ATJ graphite substrate where polycarbosilane was used as the ceramic binder are presented in Figure 17. The electrophoretic deposition bath used was Deposition Bath No. 2 in Table 2. It can be seen from Figure 17 that the thickness of the deposited ceramic layer is of the order of 20 – $30\text{ }\mu\text{m}$ and is highly porous. In Figure 17(b) and more particularly in Figure 17(c), the submicron SiC particles are visible primarily at the graphite/ceramic coating interface. At the highest magnification shown [cf., Fig. 17(c)], the bonding associated with the cross-linking of polycarbosilane after being heated at 450°C can be clearly seen. This bonding of the ceramic coating is even more evident on the surface of the deposited layer, as illustrated by the electron micrographs presented in Figure 18. Energy dispersive spectrographs taken at three different locations along the cross-section of the ceramic coating/ATJ graphite substrate, shown in Figure 17, are given in

TABLE 2. ELECTROPHORETIC BATH COMPOSITIONS, DEPOSITION CONDITIONS AND POST-DEPOSITION TREATMENTS USED IN EXPERIMENTS FOR BONDING AND DENSIFYING DEPOSITED SiC-BASED CERAMIC COATINGS ON GRAPHITE SUBSTRATES

Deposition Bath No.	Bath Composition	Deposition Conditions	Post-Deposition Treatment
1	500 ml of methanol 5 ml of water 0.10 g of $AlCl_3 \cdot 6H_2O$ 6 g of submicron SiC powder 6 g of SiC whiskers	Current density: 3 mA cm^{-2} Deposition time: 30 secs	Immersion in and/or spraying with polycarbosilane solutions or aluminum phosphate solution. Afterward some samples were subjected to high temperature treatments to bring about sintering
2	500 ml of methanol 5 ml of water 0.10 g of $AlCl_3 \cdot 6H_2O$ 6 g of submicron SiC powder 6 g of SiC whiskers 0.12 g of B_4C powder	Current density: 3 mA cm^{-2} Deposition time: 30 secs	Immersion in and/or spraying with polycarbosilane solutions or aluminum phosphate solution. Afterward some samples were subjected to high temperature treatments to bring about sintering.
3	500 ml of methanol 5 ml of water 0.10 g of $AlCl_3 \cdot 6H_2O$ 4 g of submicron SiC powder 4 g of SiC whiskers 4 g of B powder	Current density: 3 mA cm^{-2} Deposition time: 30 secs	Immersion in and/or spraying with polycarbosilane solutions or aluminum phosphate solution. Afterward some samples were subjected to high temperature treatments to bring about sintering.
4	500 ml of methanol 5 ml of water 0.10 g of $AlCl_3 \cdot 6H_2O$ 4 g of submicron SiC powder 4 g of SiC whiskers 4 g of Al powder	Current density: 3 mA cm^{-2} Deposition time: 30 secs	Immersion in and/or spraying with polycarbosilane solutions or aluminum phosphate solution. Afterward some samples were subjected to high temperature treatments to bring about sintering.

TABLE 3. POST-DEPOSITION TREATMENTS AND HIGH TEMPERATURE SINTERING CONDITIONS TO BRING ABOUT THE BONDING AND DENSIFICATION OF ELECTROPHORETICALLY DEPOSITED CERAMIC COATINGS ON GRAPHITE SUBSTRATES

POLYCARBOSILANE SOLUTIONS				
SOLUTION	SOLUTION APPLICATION	METHOD OF CURING	HIGH TEMPERATURE SINTERING CONDITIONS	
9.8 g of polycarbosilane in 150 ml of hexane	Single immersion followed by air drying.	One hour at 450°C in argon.	1. Heat to 1400°C at the rate of 5°C/min. 2. Hold at 1400°C for 1 hour.	
20 g of polycarbosilane in 150 ml of hexane	Triple immersion followed by air drying between each immersion.	One hour at 450°C in argon.	3. Raise temperature to 2150°C at the rate of 5°C/min. 4. Hold at 2150°C for 2 hours.	
30 g of polycarbosilane in 150 ml of hexane	Triple immersion followed by air drying between each immersion.	One hour at 450°C in argon.	5. Allow samples to cool down to room temperature over approximately 4 hours.	
ALUMINUM PHOSPHATE SOLUTION				
SOLUTION	SOLUTION APPLICATION	METHOD OF CURING	HIGH TEMPERATURE SINTERING CONDITIONS	
Solution consisted of by volume: 25% concentrated aluminum phosphate, 25% concentrated phosphoric acid and 50% water.	1. Coated substrate placed in a mist of solution for 2-4 seconds.	One hour at 450°C in argon.	1. Heat to 1400°C at the rate of 5°C/min. 2. Hold at 1400°C for 1 hour.	
	2. Coated substrate placed in a mist of solution for 2-4 seconds again.	One hour at 450°C in argon.	3. Raise temperature to 2150°C at the rate of 5°C/min. 4. Hold at 2150°C for 2 hours.	
	3. Coated substrate immersed in solution and allowed to soak/dry in air.	One hour at 450°C in argon.	5. Allow samples to cool down to room temperature over approximately 4 hours.	

ALUMINUM PAINT			
SOLUTION	SOLUTION APPLICATION	METHOD OF CURING	HIGH TEMPERATURE SINTERING CONDITIONS
Commercial aluminum spray paint	Coated substrates were sprayed once.	Dried in air.	<ol style="list-style-type: none"> 1. Heat to 1400°C at the rate of 5°C/min. 2. Hold at 1400°C for 1 hour. 3. Raise temperature to 2150°C at the rate of 5°C/min. 4. Hold at 2150°C for 2 hours. 5. Allow samples to cool down to room temperature over approximately 4 hours.

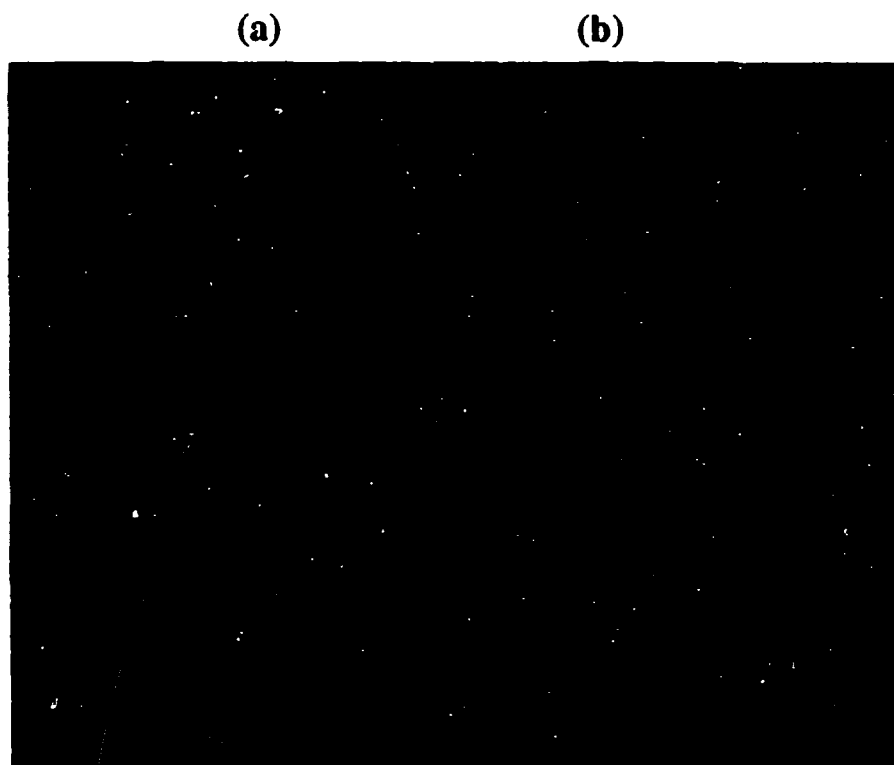


FIGURE 15. Photographic view of ceramic coated graphite substrates. Electrophoretic deposition bath contained: 6 g of submicron SiC; 6 g of SiC whiskers, and 0.12 g of B₄C. (a) bonded with polycarbosilane and (b) bonded with aluminum phosphate.

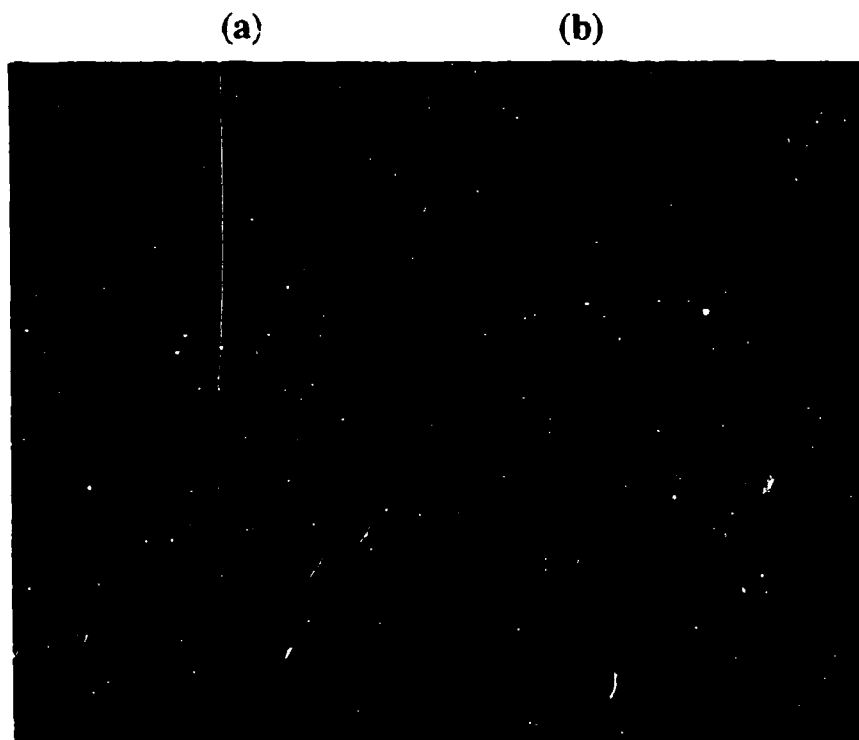
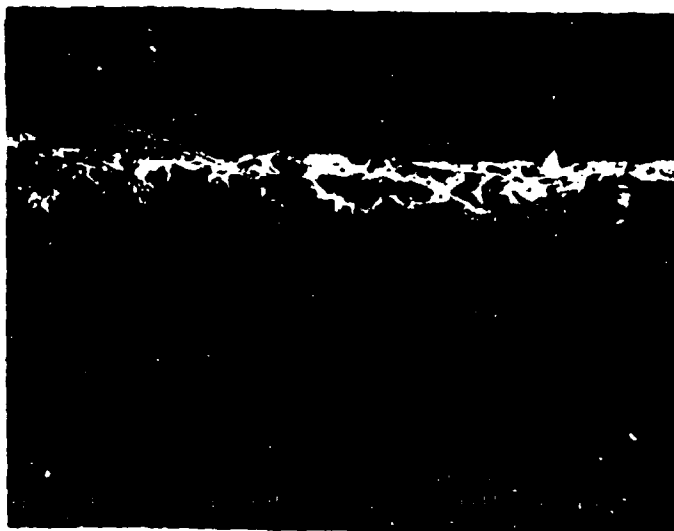
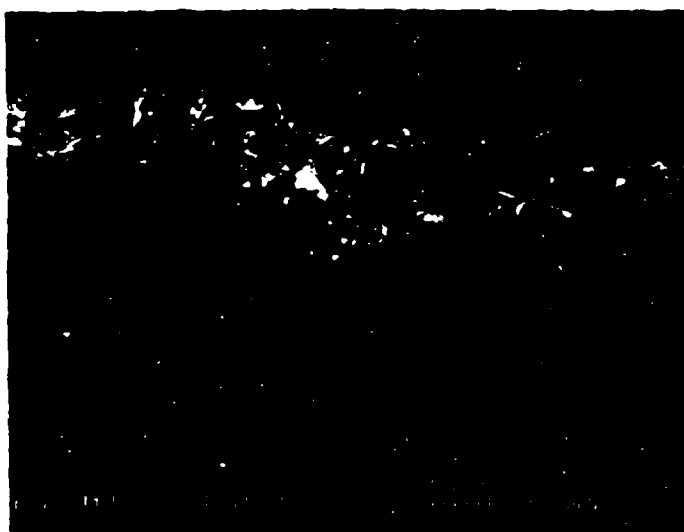


FIGURE 16. Photographic view of ceramic coated graphite substrates. Electrophoretic deposition bath contained: 4 g of submicron SiC; 4 g of SiC whiskers, and 4 g of B. (a) bonded with polycarbosilane and (b) bonded with aluminum phosphate.

(a)



(b)



(c)



FIGURE 17. Scanning electron micrographs at various magnifications of the cross-section of a ceramic coating/ATJ graphite substrate. Electrophoretic deposition bath contained: 6 g of submicron SiC; 6 g of SiC whiskers and 0.12 g of B₄C. Ceramic coating binder was polycarbosilane.

(a)



(b)

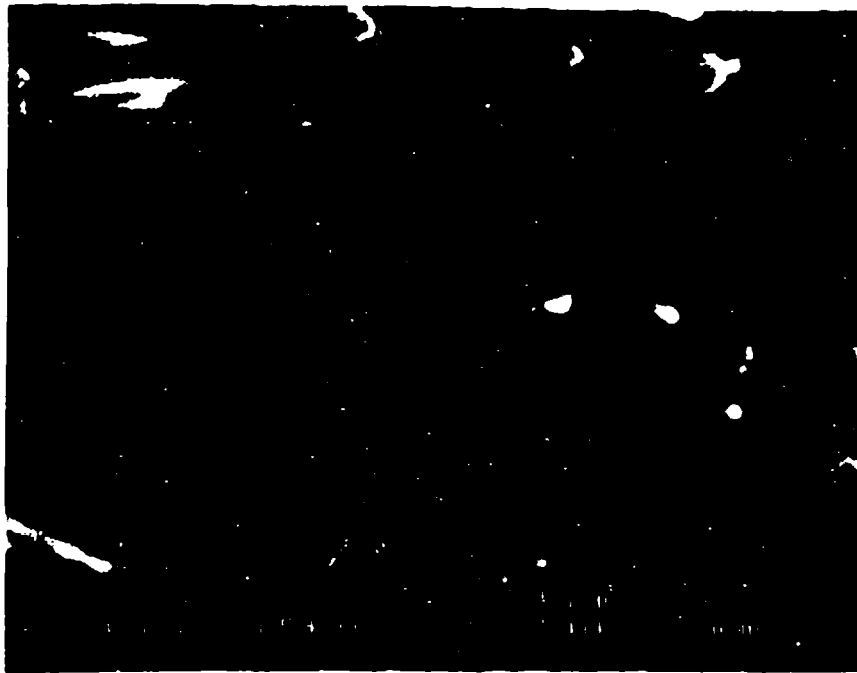


FIGURE 18. Scanning electron micrographs at various magnifications of the surface of an electrophoretically-deposited ceramic coating. Electrophoretic deposition bath contained: 6 g of submicron SiC; 6 g of SiC whiskers and 0.12 g of B₄C. Ceramic coating binder was polycarbosilane.

Figure 19. For the two spectrographs taken along the cross-section of the ceramic coating, the major peak found was due to silicon, and the minor peak due to carbon. As expected, the spectrograph taken well within the bulk of the graphite substrate yielded a peak due to carbon only.

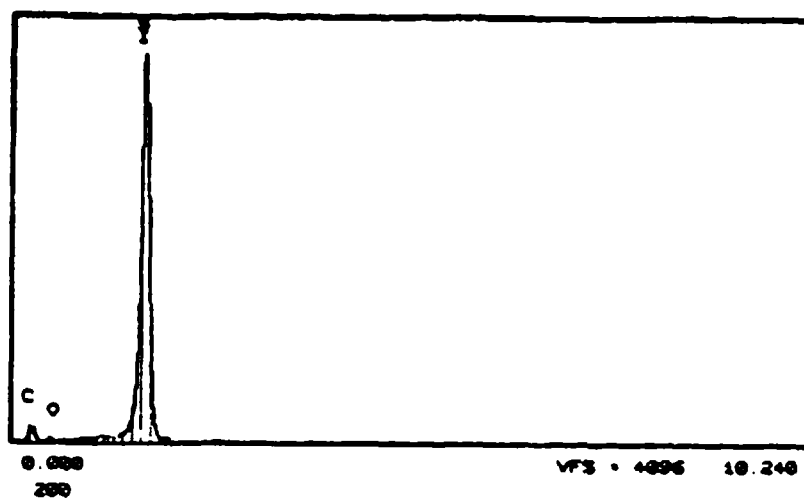
Scanning electron micrographs at various magnifications of the cross-section of a ceramic coating/ATJ graphite substrate where the coating was bonded with aluminum phosphate are presented in Figure 20. The views of the coating are similar to those already shown in Figure 17 for the related coating that was bonded with polycarbosilane. The delamination of the coating from the graphite substrate, as seen in Figure 20, is atypical of that found for electrophoretically deposited ceramic layers and is most likely due to the damage induced by the diamond saw on cutting the cross-sections. Again, submicron SiC particles at the coating/graphite interface can be clearly seen in Figure 20(c), along with the bonding brought about by the aluminum phosphate material. Scanning electron micrographs at various magnifications of the surface of the aluminum phosphate-bonded ceramic coating are presented in Figure 21. Examination of these micrographs reveals a very high degree of porosity in the coating and a high degree of bonding of the silicon carbon fibers to each other, as a result of being treated with the aluminum phosphate solution can be clearly seen. Comparison of the electron micrographs in Figure 18 with those given in Figure 21 shows that the aqueous aluminum phosphate solution penetrates the ceramic coating layer to a greater degree than the hexane solution of polycarbosilane.

Energy dispersive spectrographs taken at three different locations along the cross-section of the ceramic coating/ATJ graphite substrate shown in the electron micrographs presented in Figure 20 are given in Figure 22. For the spectrographs taken within the thickness of the ceramic coating layer [cf., Figs. 22(a) and (b)], the major peak observed is due to silicon, while minor peaks decreasing in intensity in the order phosphorous, aluminum, oxygen and carbon, can also be seen. For the electron micrograph taken within the bulk of the graphite substrate [cf., Fig. 22(c)], the only peak observed is due to carbon, as expected.

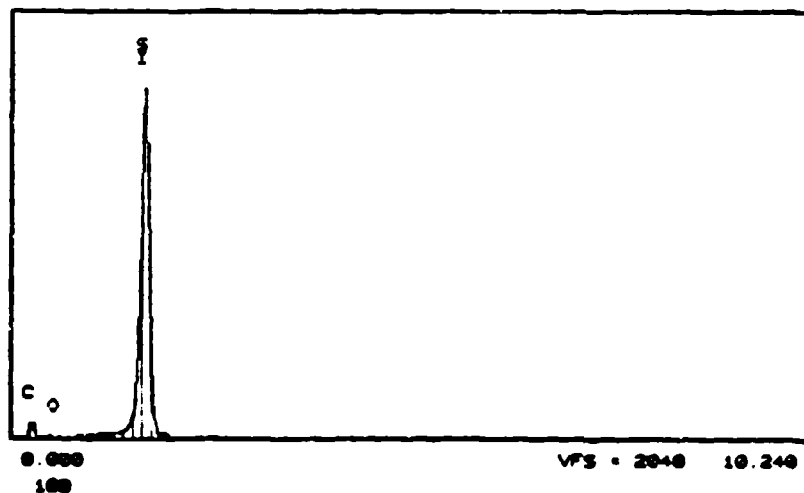
Electrophoretically deposited ceramic coatings on graphite substrates, prepared using the four electrophoretic deposition baths outlined in Table 2 and bonded using the three procedures described in Table 3, were sent to Third Millenium Technologies, Inc., for high-temperature heat treatments under inert atmospheres. The five-step heating schedule followed is outlined in Table 3. On completion of this high-temperature heat treatment, all ceramic-coated graphite samples gave no indication that any densification had occurred within the ceramic layers or that any bonding reactions had taken place between the ceramic particles and the graphite substrate. In each case a black powdery deposit on the surfaces of the graphite substrates was obtained, which could be easily wiped off. In view of the extremely high degree of porosity present in the ceramic coating layers, as indicated by the electron micrographs described earlier, the lack of ceramic coating densification is not too surprising. A suggested improvement to the approach involves the use of a lower concentration of SiC whiskers and a range of powdered SiC particle sizes.

Since poor quality ceramic coatings on graphite substrates were obtained after high temperature treatments, it was not possible to obtain cross-sections for microscopic and surface analysis. It was also not feasible to carry out oxidation and wear tests on ceramic-coated graphite coupons.

(a)



(b)



(c)

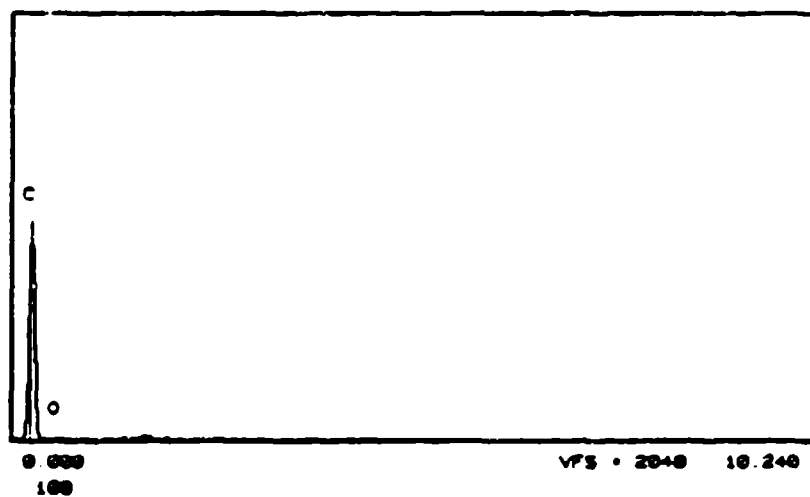
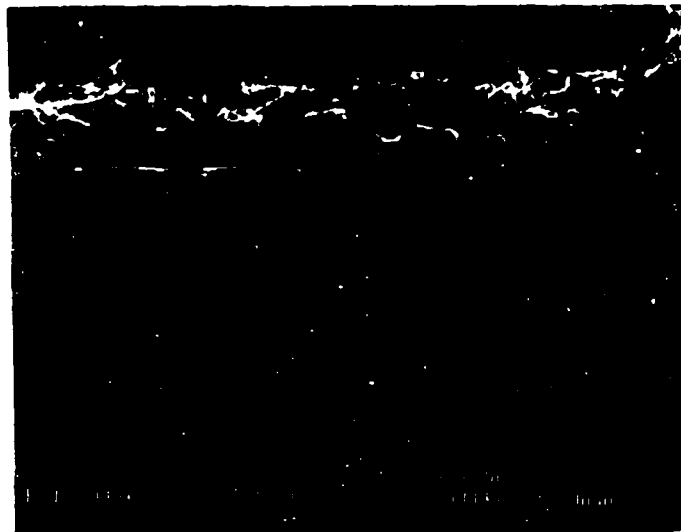


FIGURE 19. Energy dispersive spectrographs taken at three different locations along the cross-section of a ceramic coating/ATJ graphite substrate: (a) 6 μm ; (b) 13 μm ; and (c) 60 μm . Electrophoretic deposition bath contained: 6 g of submicron SiC; 6 g of SiC whiskers and 0.12g of B_4C . Ceramic coating binder was polycarbosilane.

(a)



(b)



(c)

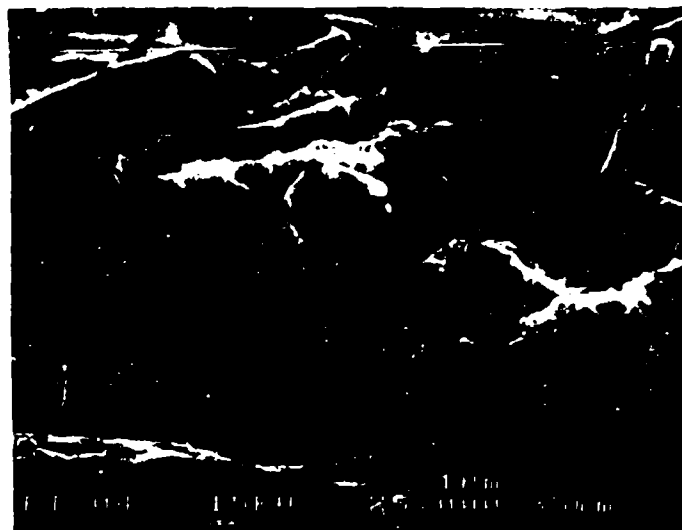
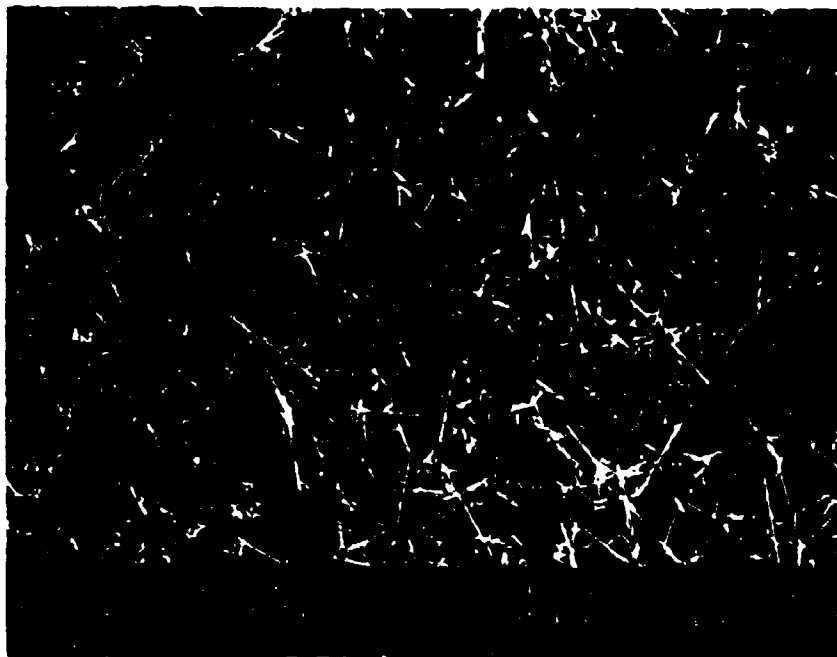


FIGURE 20. Scanning electron micrographs at various magnifications of the cross-section of a ceramic coating/ATJ graphite substrate. Electrophoretic deposition bath contained: 6 g of submicron SiC; 6 g of SiC whiskers and 0.12 g of B_4C . Ceramic coating binder was aluminum phosphate.

(a)



(b)

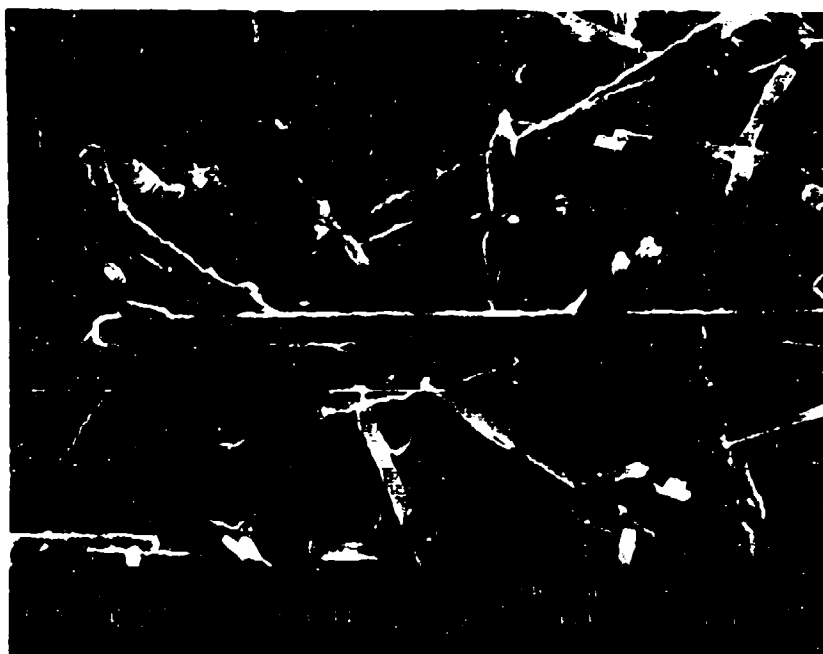
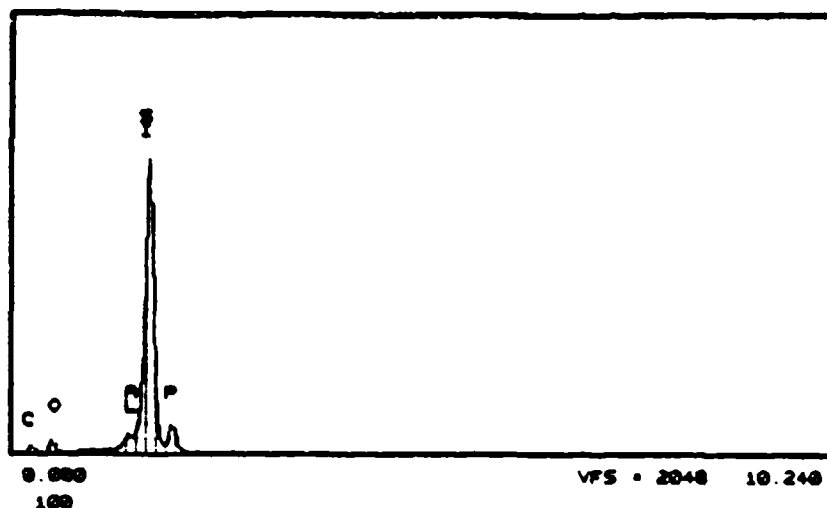
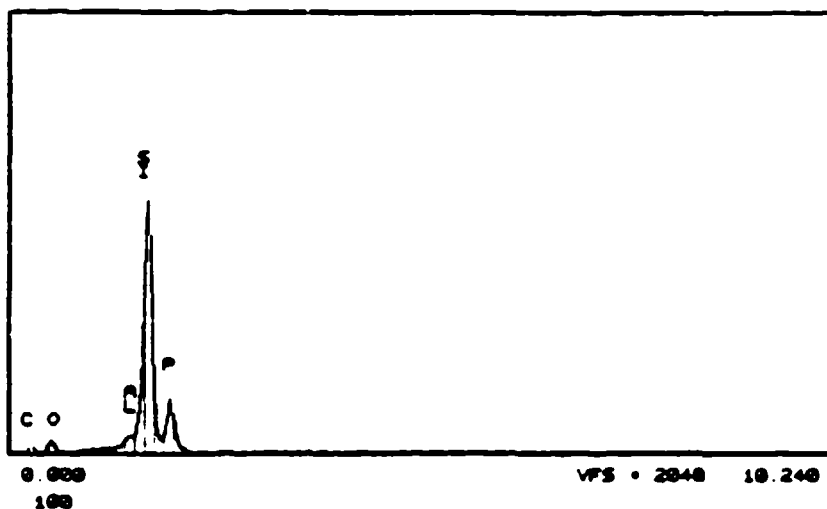


FIGURE 21. Scanning electron micrographs at various magnifications of the surface of an electrophoretically-deposited ceramic coating. Electrophoretic deposition bath contained: 6 g of submicron SiC; 6 g of SiC whiskers and 0.12 g of B₄C. Ceramic coating binder was aluminum phosphate.

(a)



(b)



(c)

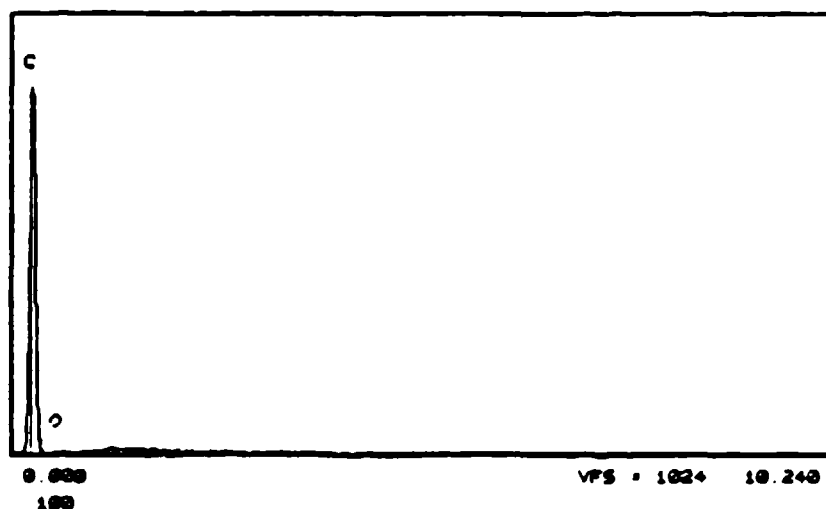


FIGURE 22. Energy dispersive spectrographs taken at three different locations along the cross-section of a ceramic coating/ATJ graphite substrate: (a) 7 μm ; (b) 12 μm ; and (c) 50 μm . Electrophoretic deposition bath contained: 6 g of submicron SiC; 6 g of SiC whiskers and 0.12g of B_4C . Ceramic coating binder was aluminum phosphate.

8. ESTIMATES OF TECHNICAL FEASIBILITY

1. It was demonstrated that a broad range of ceramic materials, including powdered and fibrous materials, can be successfully deposited on carbonaceous substrates from a methanol-based deposition bath using the electrophoretic technique.
2. Uniform, smooth and adherent ceramic coatings on graphite substrates possessing excellent throwing power were shown to be feasible using this deposition technique.
3. Coating thicknesses of at least 20–30 μm can be readily achieved using deposition times of 30 seconds or less.
4. Ceramic coatings on graphite substrates were successfully bonded using either an organometallic polymeric binder, polycarbosilane, or an inorganic binder, aluminum phosphate.
5. Lack of success on densifying ceramic coatings was attributed to the high degree of porosity remaining in bonded deposited layers. Approaches to remedy this situation were suggested.
6. Further research and development work needs to be carried out to establish the usefulness and limitations of the proposed approach for the fabrication of oxidation- and wear-resistant carbon-carbon composites.

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